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FLUORESCENCE AND THE STRUCTURE OF ORGANIC MOLECULES

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General Nature of Fluorescence

Every organic chemist is familiar with the striking green shimmer of a dilute solution of fluorescein exposed to sunlight and with similar fluorescent emissions of all colors from other compounds. Fluorescence can occur in the ultraviolet and infrared regions of the spectrum as well as in the visible. The term "fluorescence" was coined by G. G. Stokes in 1852, who related the phenomenon to a conspicuous example, that of the mineral fluorite, by analogy with the relation between opalescence and opal, but adequate understanding of the phenomenon had to await the development of modern concepts of atomic structure.

Fluorescence is the converse of the absorption of light. Both phenomena occur in their simplest forms in atomic vapors at low pressures. If a beam of white light is directed through a column of monatomic sodium vapor, spectral analysis of the transmitted beam will show two sharp absorption lines very close together, which appear dark against the bright background formed by the light from the source unabsorbed by the sodium. The illuminated vapor, observed from the side, will be seen to emit yellow light, of the same wavelength as the absorbed lines. This light, emitted in all directions, constitutes the simplest example of fluorescence. Because of the identity in wavelength between the absorbed and the emitted light, this type of fluorescence is called "resonance radiation" or "resonance fluorescence."

Under the influence of light of the appropriate wavelength, the valence electron of the sodium atom undergoes a quantum jump from the lowest energy level which it can occupy to the first of a series of excited levels, the wavelength λ_A being determined by the condition that the corresponding quantum of energy, hc/λ_A (where h is Planck's constant and c is the velocity of light), be just sufficient to supply the energy excess of the excited, over the normal, electronic state. (In the case of the sodium atom, the excited level happens to consist of two levels close together in energy, hence the doublet nature of the absorption and fluorescence spectra.) The atom cannot stay in the excited state very long; if the excited atom collides with another atom or with the walls of the containing vessel, the extra energy is likely to be dissipated as heat, but if no such collision occurs within about 10^{-8} sec., the excitation energy will be lost as a quantum of radiation, which constitutes the resonance fluorescence.

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For molecules in solution, instead of a single line, the absorption spectrum corresponding to a single electronic transition may consist of a series of bands of diminishing wavelength, corresponding to transitions to higher and higher states of vibrational energy associated with the excited electronic state. The well-known ultraviolet band spectrum of benzene is an example. Most electronically excited molecules in solution dissipate their excitation energy as heat, by collision with solvent molecules or by other processes, and fluorescent re-emission of the absorbed energy is relatively rare; when it occurs, it is of structural significance. Among fluorescent molecules in solution, any vibrational energy acquired in the absorption process is invariably lost by collision with solvent molecules, and only transitions from the nonvibrating upper electronic state to various vibrational states of the ground electronic state are concerned in fluorescence. The condition for fluorescence in solution is, therefore, that the vibrationally unexcited upper electronic state be able to survive all the deactivating processes to which it may be exposed in the period of about 10^{-8} to 10^{-6} sec. which elapses between the absorption transition and fluorescent emission. Figure 1 illustrates these details of the absorption and fluorescence processes. Fluorescent transitions to excited vibrational states of the

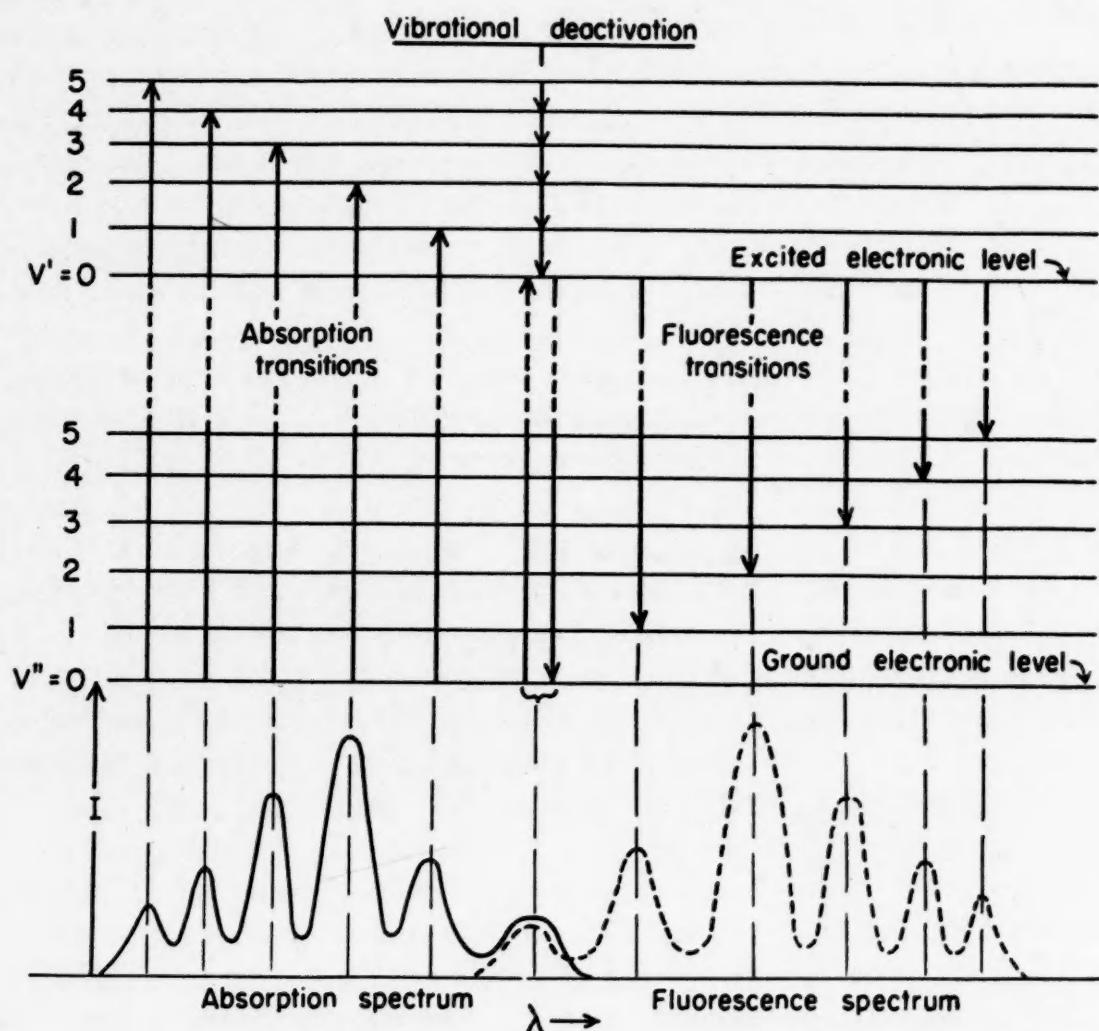


Fig. 1. Molecular absorption and fluorescence processes. Absorption transitions from the vibrationless ground state to various vibrationally excited states of the upper electronic level are on the left; within 10^{-8} sec., vibrational deactivation of the excited state occurs in solution, and, after about 10^{-8} sec., the fluorescent transitions to various vibrational states of the ground electronic level take place. The corresponding absorption and fluorescence spectra are shown below the respective transitions.

ground electronic state cause the emission of radiation of longer wavelength than that absorbed, a general characteristic of fluorescence in solution. This batho-

chromic displacement of the fluorescence spectrum from the absorption spectrum is called the Stokes shift, after its discoverer. There is often an approximate mirror-image relation between the absorption and the fluorescence spectra, as shown in Figure 1.

Fluorescence and Structure

It may clarify the structural requirements of a fluorescent molecule to consider the nature of some of the deactivating processes which prevent most molecules from fluorescing. Collisional deactivation of the excited molecules with solvent molecules is a possibility, but probably not the reason for lack of fluorescence in the common solvents, such as water, alcohol, ether, etc. The first excited electronic level of these solvent molecules is too high in energy to allow electronic excitation by collision with excited solute molecules absorbing visible or near-ultraviolet radiation, and collisional dissipation of the excitation energy of the solute could affect only the translational and vibrational motion of the solvent, by an inefficient interaction. In certain cases, however, electronic energy can be transferred from an excited molecule to a solvent molecule, possibly causing decomposition of the latter.

Deactivating processes within the electronically excited molecule seem to be the principal reason for lack of fluorescence. If the absorption act is itself directly accompanied by a decomposition of the molecule (signaled by its exhibiting a continuous absorption spectrum, without vibrational structure, even at low pressure), no fluorescence will occur, but it may also happen that, although the molecular configuration of the excited molecule at the instant of its formation is stable, unstable configurations leading to the breaking of a bond may occur before the fluorescent emission has time to take place (1), and the molecule would then be non-fluorescent because of internal conversion of the excitation energy. If the electronic energy of a polyatomic molecule is much greater than the bond strength of the weakest linkage, the probability of internal conversion (predissociation) will be relatively high.

A consequence of this latter circumstance is that fluorescence is rare among compounds whose absorption bands are in the short-wavelength ultraviolet region. Butadiene, whose longest wavelength absorption band is about 2200 Å., is not fluorescent in the ultraviolet, but decapentacene derivatives, containing five conjugated acyclic double bonds, absorb and fluoresce in the visible region, for which the electronic energy of the excited state is below the bond energy of any atom in the molecule. Benzene, the long-wavelength limit of whose ultraviolet absorption corresponds to an excitation energy of about 106 kcal. per mole, emits an ultraviolet fluorescence spectrum, the excitation energy being less than that required to separate the first hydrogen atom from the molecule, and considerably below that required to break a carbon-carbon bond. Iodobenzene and nitrobenzene are not fluorescent. The energy required to separate the iodine atom from iodobenzene is about 55 kcal. per mole and, to separate the nitro group, about 62 kcal. per mole, both considerably below the electronic energy acquired by absorption.

If, however, a molecule containing iodine or the nitro group absorbs at a sufficiently long wavelength, its capacity to fluoresce may not be entirely destroyed. Erythrosin, for example, fluoresces in spite of its four iodine atoms, its long-wavelength absorption edge corresponding to an excitation energy not quite sufficient to break the carbon-iodine bond. Similarly, nitrodimethylaniline and some nitrated dyes fluoresce—the absorption bands are in the visible region and the excitation energy is not in excess of that required to separate the nitro group. But, in general,

fluorescence of nitro- or iodo-compounds is weak, as if there were some dissipative electronic interaction between the chromophore and these groups other than breaking of bonds.

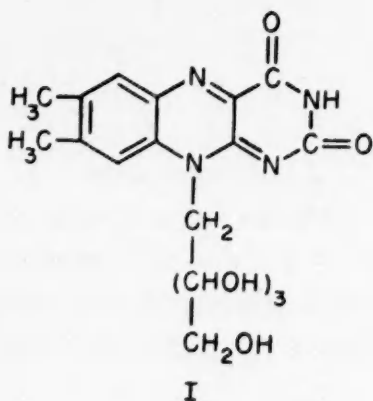
These internal dissipative processes are inhibited by lowering the temperature and increasing the viscosity of the solvent, and hence the intensity of fluorescence is frequently increased in solvents like glycerol at low temperature, or in glasses, such as boric oxide, or a mixture of alcohol, ether, and pentane frozen by liquid nitrogen. Hydrogen-bonding of the fluorescent molecule with solvent molecule may possibly participate in this effect. Adsorption to a surface may have a similar effect to lowering the temperature or increasing the viscosity; azo dyes, for example, mostly nonfluorescent in solution, may fluoresce brightly when adsorbed on a fabric.

In the light of the previous discussion, one can understand why fluorescence is rare among acyclic compounds, such as saturated hydrocarbons, alcohols, acids, esters, ethers, etc., and among unsaturated compounds of short chain length. If, however, an acyclic conjugated chain is long enough to bring its absorption into the visible or near-ultraviolet region, and the molecule contains no weak bond or other interfering structure, normal fluorescence is to be expected. Acetone, absorbing at about 2700 Å., is photoluminescent, but part of the emission is due to biacetyl formed by photochemical decomposition of the acetone.

The series of linearly annulated aromatic hydrocarbons from benzene to pentacene exhibit fluorescence in dilute solution and in the solid state, of regularly increasing wavelength, in step with the absorption spectra; the fluorescence of benzene and naphthalene is limited to the ultraviolet region, while that of anthracene, naphthacene, and pentacene shows regularly deeper visible colors. Hydrogenation of condensed ring hydrocarbons at sites which break the conjugation between the rings may cause visible fluorescence to disappear, as the absorption spectrum retreats into the ultraviolet. For example, the blue fluorescence of anthracene is lost in 9,10-dihydroanthracene, whose absorption and fluorescence spectra, consistent with its structure, resemble those of benzene.

Substituents alter the fluorescence of their parent compounds both by effects on the position and intensity of absorption and on the quantum yield of fluorescence. As has been mentioned, loosely bound groups, like -I, -NO, or NO₂, inhibit fluorescence, while stable groups, such as NH₂, -OH, or -O-, which cause bathochromic shifts in absorption, also shift fluorescence to longer wavelength and intensify the emission.

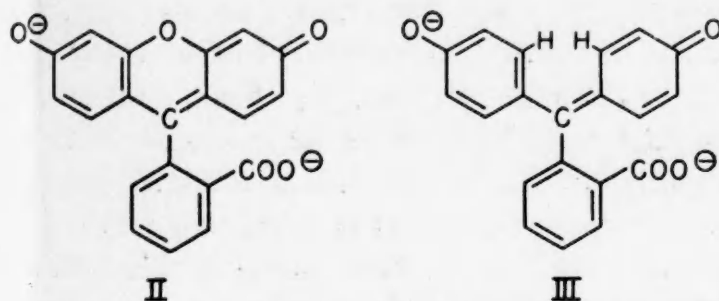
Compact heterocyclic nuclei, such as quinoline, isoquinoline, indole, acridine, carbazole, and some pyrimidines, purines, and nucleic acids are fluorescent. The fluorescence of riboflavin (I) and of related compounds is important in their characterization.







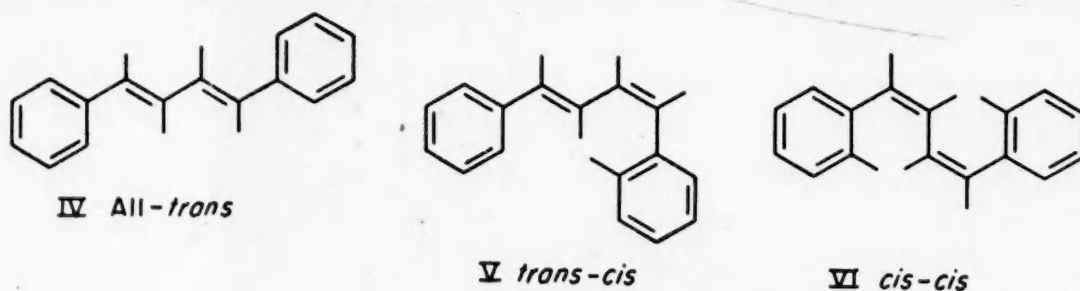
Since R. Meyer, one of the earliest workers on the relation between fluorescence and chemical constitution, contrasted the strong, visible fluorescence of the fluorescein ion (II) with its absence in the strongly colored phenolphthalein (III), it has been realized that ring closure is conducive to fluorescence. It seems likely that



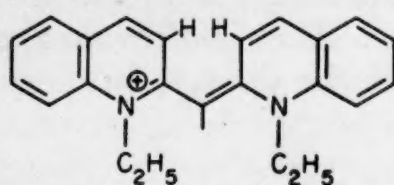
the strong fluorescence of certain metal chelate compounds in comparison with their parent molecules is another example of the effect of ring closure; the Zn, Cd, and Mg salts of 8-hydroxyquinoline, in colloidal suspension, are much more brightly fluorescent than 8-hydroxyquinoline itself.

It will be noted that the nonfluorescent member of the pair just mentioned exhibits crowding between the hydrogen atoms indicated in the formula, tending to prevent the attainment of a planar configuration of the chromophoric atoms. In (II), the atoms in the chromophore, which comprises the assembly of π -electrons between the terminal oxygen atoms, are coplanar, but the third benzene ring is probably forced out of the chromophoric plane. It seems likely, however, that nonplanarity not involving the chromophore may have only a minor effect on the absorption and fluorescence, but crowding and noncoplanarity of the atoms in the chromophore strongly tend to destroy the capacity to fluoresce. Torsional vibrations are possible in the nonplanar molecules, which appear to be particularly effective in degrading electronic excitation energy. This effect of nonrigidity in destroying the ability of a molecule to fluoresce was emphasized by Lewis and Calvin (2), who likened the radiationless dissipation of electronic energy within a nonrigid molecule to the effect of a loose bolt in a mechanical structure.

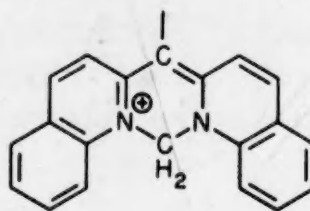
Cis- and *trans*-isomers frequently differ markedly in fluorescence; for example, *cis*-stilbene fluoresces feebly in comparison with the *trans*-compound. Here again, the effect of crowding and nonplanarity is evident. Similarly, among the diphenylbutadienes, Sandoval and Zechmeister (3) found the extended, noncrowded *trans-trans* form (IV) to be strongly fluorescent and to exhibit well-resolved vibrational structure in its absorption spectrum, while the crowded *cis*- forms (V and VI) were less strongly fluorescent and showed more poorly resolved absorption-band structure.



A final example illustrating various factors affecting fluorescence is offered by the cyanine dyes. The cation of the dye, 1,1'-diethyl-2,2'-cyanine (VII), does not fluoresce in alcohol, probably because of some crowding between the 3 and 3' hydrogen atoms, but the compact 1,1'-methylene-2,2'-cyanine (VIII) is fluorescent in alcohol.



VII



VIII

Increasing the chain length, however, of the methine bridge in (VII) by one vinyl group gives a compound which is fluorescent in alcohol, because of the relief from crowding thereby effected (4). In concentrated aqueous solution, (VII) forms an aggregate in which the molecules are piled up somewhat like the cards in a pack (although each molecule is probably bent slightly). This aggregate is strongly fluorescent, and, in fact, aggregates of this type are unique in organic chemistry, in showing a fluorescence spectrum of nearly the same wavelength as the absorption spectrum (5). The appearance of fluorescence in the aggregate is probably partly caused by the constraints introduced by the intermolecular forces in suppressing the motions responsible for internal dissipation in the monomeric form of the dye.

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